

# **LIQUID DISPENSING METHOD AND SYSTEM WITH HEADSPACE GAS REMOVAL**

## **BACKGROUND OF THE INVENTION**

5           The present invention relates to a storage and dispensing system for the storage and dispensing of liquids. In particular, the present invention relates to a method and system for dispensing liquid to a manufacturing process from a container including a headspace gas.

          Certain manufacturing processes require the use of liquid  
10 chemicals such as acids, solvents, bases, photoresists, dopants, inorganic solutions, organic solutions, biological solutions, pharmaceuticals, and radioactive chemicals. Storage and dispensing systems allow alternative containers to be used to deliver liquid chemicals to a manufacturing process at a specified time. These process liquids are usually dispensed from pressurized  
15 storage and dispensing containers by special dispensing pumps.

          After filling these containers at a filling facility, the containers are typically shipped to a location for use in a manufacturing process. Once at the manufacturing process facility, these containers may be stored for an extended period of time before being connected to a manufacturing process.  
20 However, the purity of some of the above-listed chemicals has a tendency to decay when stored for an extended period of time. For example, in the manufacture of thin film transistor flat panel displays, the color filter chemical used tends to decay as free radicals in the color filter chemical are released during shipment and storage as a result of temperature fluctuations. To prevent  
25 this from occurring, an empty portion of the container, referred to as the headspace, is filled with a headspace gas. The headspace gas prevents the decay of the liquid chemical by inhibiting chemical reactions from occurring in the liquid during storage. For example, in the case of the color filter chemical, a headspace gas including oxygen is introduced into the container at the filling  
30 facility, since oxygen has a tendency to scavenge free radicals in the chemical as they are released, thereby preventing the decay of the color filter chemical.

When the container is to be connected to the manufacturing process, the headspace gas is no longer needed or desired. Thus, the headspace gas must be removed prior to dispensing the liquid to the manufacturing process. However, caution must be exercised to avoid agitating the container or forcing  
5 the headspace gas into the liquid chemical while draining the headspace gas. The introduction of gas into the liquid chemical may result in the formation of air bubbles in the chemical, which can render the liquid chemical defective for use in the manufacturing process.

Furthermore, it may be desired to leave a small amount of gas in  
10 the container after removal of the headspace gas. When all of the liquid has been dispensed from the container, this small amount of empty detect gas is detected by the dispenser to indicate that the container is empty. In conventional systems, the amount of empty detect gas remaining in the container is not easily controllable.

15 Thus, a system that allows for easy removal of headspace gas and, if desired, easy regulation of the amount of empty detect gas remaining in the container after headspace gas removal is desirable.

## BRIEF SUMMARY OF THE INVENTION

The present invention is a method and system for dispensing liquid chemical to a manufacturing process from a container including an outer container and an inner container, a portion of the inner container occupied by the liquid chemical, a remainder of the inner container occupied by a headspace gas. The system includes a probe having a flow passage therein insertable into an interior of the inner container, and a gas passage communicating between the interior of the inner container and an exterior of the outer container. The system further includes means in fluid communication with a space between inner walls of the outer container and the inner container for permitting fluid under pressure to flow into the space between the inner walls of the outer container and the inner container to force the headspace gas out of the inner container via the gas passage to a headspace gas drain and to force liquid out of the inner container through the flow passage in the probe to the manufacturing process.

In a preferred embodiment, the system further includes a drain valve connected between the headspace gas drain and the gas passage. The drain valve has an open position selectable to allow the headspace gas to evacuate to the headspace gas drain via the gas passage. The drain valve also has a closed position selectable when the headspace gas has been exhausted from the interior of the inner container. The system also preferably includes a liquid sensor connected between the gas passage and the headspace gas drain to sense when liquid chemical begins to flow in the gas passage to indicate that the headspace gas has been exhausted from the interior of the inner container.

The system also preferably includes an empty detect means for detecting when the liquid chemical has been exhausted from the inner container. In one embodiment, the empty detect means is an empty detect gas sensor. In use, a small amount of empty detect gas is introduced to an interior of the inner container immediately prior to dispensing of the liquid chemical to the manufacturing process. The empty detect gas sensor senses this empty detect gas when the liquid chemical has been exhausted from the container. When the

- empty detect gas is sensed by the empty detect gas sensor, dispensing of liquid to the manufacturing process is terminated. In another embodiment, the empty detect means includes a scale for weighing the fluid container while the liquid is dispensed to the manufacturing process such that dispensing of the liquid is
- 5 terminated when the fluid container reaches a predetermined empty weight as measured by the scale.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of a system according to a preferred embodiment of the present invention for dispensing liquid to a manufacturing process from a container including a headspace gas provided to stabilize the liquid during shipment and storage of the container.

FIG. 2 is a schematic of a system according to another preferred embodiment of the present invention for dispensing liquid to a manufacturing process from a container including a headspace gas provided to stabilize the liquid during shipment and storage of the container.

## DETAILED DESCRIPTION

FIG. 1 is a schematic of system 10 according to a preferred embodiment of the present invention for dispensing liquid 12 to manufacturing process 13 from container 14 including headspace 16 filled with headspace gas 18. Container 16 includes flexible inner container 20 and rigid outer container 22. System 10 further includes compression air or nitrogen supply 30, compression air passage 32, headspace gas passage 34, drain valve 36, liquid sensor 38, headspace gas drain 40, flow passage 42, container scale 44, and system control 46.

Compression air supply 30 is connected to compression space 31 (i.e., the space between inner walls of outer container 22 and outer surfaces of the inner container 20) via compression air passage 32. The interior of inner container 20 is connected to headspace gas drain 40 via gas passage 34. Drain valve 36 and liquid sensor 38 are connected along gas passage 34 between the interior of inner container 20 and headspace gas drain 40. Finally, the interior of inner container 20 is in fluid communication with manufacturing process 13 via flow passage 42.

Gas passage 34 and flow passage 42 are preferably combined in a single connector package such that the interior of inner container 20 comes into fluid communication with headspace gas drain 40 and manufacturing process 13 with one connection. Flow passage 42 is typically provided in a probe that is insertable through a port of the container and into inner container 20 to provide fluid communication between liquid 12 and manufacturing process 13.

Outer container 22 provides the mechanical support and protection required by flexible inner container 20 (e.g., a flexible polymeric bag) during filling, transport, handling, and dispensing. Outer container 22 is typically constructed of metal, although other materials, including plastic materials, may also be used, depending upon government regulatory specifications for handling of the particular liquid to be contained within container 14. Preferably, container 14 is a container as shown in U.S. Pat. No.

5,335,821 to Osgar issued on August 9, 1994, which is herein incorporated by reference.

System control 46, which is preferably a microprocessor-based control system, is connected to compression air supply 30, drain valve 36, liquid  
5 sensor 38, and container scale 44. System control 46 controls operation of system 10 based upon signals received from the various components of system 10.

Prior to attachment to manufacturing process 13, container 14 is filled at a filling facility. During filling, inner container 20 is first inflated with  
10 a gas such as nitrogen. Liquid 12 is then introduced through a port in container 14 to fill inner container 20 within outer container 22.

The purity of some chemicals has a tendency to decay when stored for an extended period of time, especially when subjected to temperature fluctuations. For example, in the manufacture of thin film transistor flat panel  
15 displays, the color filter chemical used tends to decay or cross-link as free radicals in the color filter chemical are released during shipment and storage. To prevent this from occurring, an empty portion of the container, headspace 16, is filled with headspace gas 18. Headspace gas 18 prevents the decay of liquid 12 by inhibiting chemical reactions from occurring in liquid 12 during shipment  
20 and storage of container 14. For example, in the case of the color filter chemical, a headspace gas 18 including oxygen is introduced into inner container 20 at the filling facility, since oxygen has a tendency to scavenge free radicals in the chemical as they are released, thereby preventing the decay or cross-linking of the color filter chemical.

25 When container 14 is to be connected to manufacturing process 13, headspace gas 18 is no longer needed or desired. Thus, headspace gas 18 must be removed prior to dispensing liquid 12 to manufacturing process 13. To begin, compression air passage 32, gas passage 34, and flow passage 42 are connected to container 14. A signal is then sent by system control 46, which is  
30 preferably a microprocessor-based system, to open drain valve 36. This

produces a fluidic connection between the interior of inner container 20 and headspace gas drain 40. Subsequently, pressurized fluid, preferably compressed air or nitrogen, is supplied to compression space 31 by compression air supply 30 to force headspace gas 18 through gas passage 34, through liquid sensor 38, and to headspace gas drain 40. As headspace gas 18 is withdrawn from inner container 20 of container 14, air is permitted to enter compression space 31, thereby collapsing flexible inner container 20. While inner container 20 is preferably collapsed with pressurized air, any means capable of collapsing inner container 20 to force headspace gas 18 through gas passage 34 may be used, including hydraulic or mechanical based devices. Alternatively, a pump connected to gas passage 34 can withdraw headspace gas 18 from container 14.

After headspace gas 18 has been exhausted from inner container 20, liquid 12 begins to flow in gas passage 34 as compressed air supply 30 continues to supply air to compression space 31. When liquid 12 reaches liquid sensor 38, a signal is sent to system control 46 to close drain valve 36. This terminates the connection between the interior of inner container 20 and headspace gas drain 40. Alternatively, a user of system 10 may visually determine when liquid 12 begins to flow in gas passage 34 and manually turn off drain valve 36 to terminate the connection to headspace gas drain 40.

When the connection between the interior of inner container 20 and headspace gas drain 40 has been terminated, liquid 12 is forced up through flow passage 42 as compressed air continues to be supplied to compression space 31 by compressed air supply 30. As liquid 12 is withdrawn from flexible inner container 20 of container 14, air is permitted to enter compression space 31, thereby collapsing inner container 20. While inner container 20 is preferably collapsed with pressurized air, any means capable of collapsing inner container 20 to force liquid through flow passage 42 may be used, including hydraulic or mechanical based devices. Alternatively, a pump or venturi connected to flow passage 42 can withdraw liquid 12 from container 14.



At this point, it is important to note that had headspace gas 18 not been removed prior to dispensing liquid 12 to manufacturing process 13, headspace gas 18 would begin to dissolve into solution pursuant to Henry's law. Henry's law states that, at a constant temperature, the amount of gas dissolved in a solution is directly proportional to the pressure of the gas above the solution. Thus, because inner container 20 is collapsed by compressed air supply 30 to force liquid 12 out of inner container 20, the pressure of headspace gas 18 would increase during this process. This would cause headspace gas 18 to dissolve into liquid 12, thereby resulting in deleterious bubble formation when liquid 12 is delivered to process 13.

As liquid 12 is being dispensed to manufacturing process 13, the weight of container 14 decreases. Container scale 44 continually weighs container 14 as liquid 12 is dispensed to manufacturing process 13 to determine when container 14 reaches a predetermined empty weight. The empty weight of container 14 is the weight of outer container 22 with an empty inner container 20 inside. The determination of the empty weight by container scale 44 assures that all of liquid 12 is dispensed from inner container 20.

When container scale 44 determines that container 14 is empty, system control 46 sends a signal to turn off compression air supply 30. Subsequently, compression air passage 32, gas passage 34, and flow passage 42 are disconnected from empty container 14, empty container 14 is removed from system 10, and a new container 14 containing liquid 12 and headspace gas 18 is connected to system 10. Dispensing of liquid 12 from container 14 then recommences.

FIG. 2 is a schematic of system 50 according to another preferred embodiment of the present invention for dispensing liquid 12 to manufacturing process 13 from container 14. Container 14 includes headspace gas 18 provided to stabilize liquid 12 during shipment and storage of container 14. Container 16 includes flexible inner container 20 and rigid outer container 22. Similar to system 10 shown in FIG. 1, system 50 includes compression air supply 30,

compression air passage 32, headspace gas passage 34, liquid sensor 38, headspace gas drain 40, flow passage 42, and system control 46. Additionally, system 50 includes empty detect gas supply 52, regulator gauge 54, first block valve 55, gas quantity controller 56, second block valve 58, select valve 60, and  
5 empty detect gas sensor 62.

Compression air supply 30 is connected to compression space 31 via compression air passage 32. Select valve 60 is a three-port valve connecting the interior of inner container 20 (via gas passage 34) to the devices connected to select valve port 60a or select valve port 60b, depending on the position state  
10 of select valve 60. More specifically, in a first position select valve 60 provides a fluidic connection between the interior of inner container 20 and the devices connected to port 60a (i.e., liquid sensor 38 and headspace gas drain 40). Liquid sensor 38 is connected between select valve 60 and headspace gas drain 40. In a second position, select valve 60 provides a fluidic connection between the  
15 interior of inner container 20 and the devices connected to port 60b (i.e., empty detect gas supply 52, regulator gauge 54, first block valve 55, gas quantity controller 56, and second block valve 58). Regulator gauge 54, first block valve 55, gas quantity controller 56, and second block valve 58 are connected between empty detect gas supply 52 and select valve 60. Finally, the interior of inner  
20 container 20 is in fluid communication with manufacturing process 13 via flow passage 42. Empty detect gas sensor 62 is connected along flow passage 42.

Gas passage 34, flow passage 42, and select valve 60 are preferably combined in a single connector package such that the interior of inner container 20 is connected to headspace gas drain 40, empty detect gas supply 52,  
25 and manufacturing process 13 with one connection. Flow passage 42 is typically provided in a probe that is insertable through a port of the container and into inner container 20 to provide fluid communication between liquid 12 and manufacturing process 13.

In the embodiment shown in FIG. 2, system control 46 is  
30 connected to compression air supply 30, liquid sensor 38, regulator gauge 54,

first block valve 55, second block valve 58, select valve 60, and empty detect gas sensor 62. System control 46 controls operation of system 50 based upon signals received from the various components of system 50.

As described above, when container 14 is to be connected to manufacturing process 13, headspace gas 18 is no longer needed or desired. Thus, headspace gas 18 must be removed prior to dispensing liquid 12 to manufacturing process 13. The procedure of removing headspace gas 18 from container 14 in system 50 is similar to the same process in system 10. To begin, compression air passage 32, gas passage 34, and flow passage 42 are connected to container 14. System control 46 then sends a signal select valve 60 to turn to its first position to produce a fluidic connection between the interior of inner container 20 and headspace gas drain 40 (via select valve port 60a). A user of system 50 may also manually turn select valve 60 to its first position. Subsequently, pressurized fluid, preferably compressed air or nitrogen, is supplied by compressed air supply 30 to compression space 31 to force headspace gas 18 through gas passage 34, through liquid sensor 38, and to headspace gas drain 40. As headspace gas 18 is withdrawn from inner container 20 of container 14, air is permitted to enter compression space 31, thereby collapsing flexible inner container 20. While inner container 20 is preferably collapsed with pressurized air, any means capable of collapsing inner container 20 to force headspace gas 18 through gas passage 34 may be used, including hydraulic or mechanical based devices. Alternatively, a pump or venturi connected to gas passage 34 can withdraw headspace gas 18 from container 14.

After headspace gas 18 has been exhausted from inner container 20, liquid 12 begins to flow in gas passage 34 as compressed air supply 30 continues to supply air to compression space 31. When liquid 12 reaches liquid sensor 38, system control 46 responds by turning select valve 60 to the second position. This terminates the connection between the interior of inner container 20 and headspace gas drain 40, and opens the connection between the interior of inner container 20 and select valve port 60b. Alternatively, a user of system 50

may visually determine when liquid 12 begins to flow in gas passage 34 and manually turn select valve 60 to the second position to terminate the connection to headspace gas drain 40.

At this point, it is important to note again that, had headspace gas 18 not been removed prior to dispensing liquid 12 to manufacturing process 13, headspace gas 18 would begin to dissolve into solution pursuant to Henry's law. Because inner container 20 is collapsed by compressed air supply 30 to force liquid 12 out of inner container 20, the pressure of headspace gas 18 would increase during this process. This would cause headspace gas 18 to dissolve into liquid 12, thereby resulting in deleterious bubble formation in liquid 12 as it is delivered to process 13.

In many liquid dispense systems, it is desirable to leave a small amount of gas in container 14 after removal of headspace gas 18. When all of liquid 12 has been dispensed from container 14, this small amount of gas, referred to as empty detect gas, is detected by a sensor (for example, empty detect gas sensor 62 in FIG. 2) to indicate that the container is empty. In conventional systems, the amount of empty detect gas remaining in container 14 is not easily controllable, since the amount of gas being exhausted to headspace gas drain 40 is not easily measurable.

In system 50, the addition of empty detect gas into inner container 20 is controlled by empty detect gas supply 52, regulator gauge 54, first block valve 55, gas quantity controller 56, and second block valve 58. To begin, system control 46 opens first block valve 55 to produce a fluidic connection between empty detect gas supply 52 and gas quantity controller 56. Empty detect gas then begins to flow into gas quantity controller 56 from empty detect gas supply 52. As gas quantity controller 56 fills with empty detect gas, the pressure in gas quantity controller 56 increases. The pressure is regulated by regulator gauge 54 and may be measured by a pressure transducer integrated into gas quantity controller 56. The amount of empty detect gas that flows into gas quantity controller 56 depends on the capacity volume of gas quantity

controller 56 and the pressure of the empty detect gas in gas quantity controller 56. Based on these factors, empty detect gas supply 52 continues to flow until gas quantity controller 56 is filled with the desired amount of gas (e.g., 100 pounds per square inch gauge).

5                   When the desired amount of gas has filled gas quantity controller 56, system control 46 closes first block valve 55 to terminate the connection between empty detect gas supply 52 and gas quantity controller 56. Subsequently or simultaneously, system control 46 opens second block valve 58 to produce a fluidic connection between gas quantity controller 56 and the  
10 interior of inner container 20. This allows the empty detect gas contained in gas quantity controller 56 to flow into the interior of inner container 20. If compression air supply 30 is turned off while empty detect gas flows from gas quantity controller 56 into inner container 20, the empty detect gas contained in gas quantity controller 56 will flow into inner container 20. If compression air  
15 supply 30 remains active while empty detect gas flows from gas quantity controller 56 into inner container 20, empty detect gas will flow from gas quantity controller 56 into inner container 20 until an equilibrium pressure is reached between compression air supply 30 and the pressure in gas quantity controller 56. Typically, whether compression air supply 30 is active is  
20 controlled by a two-way or a three-way valve connected between compression air supply 30 and compression space 31. In general, the amount of empty detect gas that flows from gas quantity controller 56 into inner container 20 is based on the size of gas quantity controller 56, the difference in pressure between gas quantity controller 56, and the pressure in compression space 31.

25                   After empty detect gas has stopped flowing from gas quantity controller 56, system control 46 closes second block valve 58 to terminate the connection from gas quantity controller 56 to inner container 20. After second block valve 58 is closed, liquid 12 is forced up through flow passage 42 as compressed air is supplied to compression space 31 by compressed air supply  
30 30. As liquid 12 is withdrawn from flexible inner container 20 of container 14,

air is permitted to enter compression space 31, thereby collapsing inner container 20. While inner container 20 is preferably collapsed with pressurized air, any means capable of collapsing inner container 20 to force liquid through flow passage 42 may be used, including hydraulic or mechanical based devices.

5 Alternatively, a pump or venturi connected to flow passage 42 can withdraw liquid 12 from container 14.

As inner container 20 is collapsed by compression air supply 30, liquid 12 continues to flow to manufacturing process 13 until liquid 12 is exhausted from inner container 20. After liquid 12 has been exhausted from  
10 inner container 20, only the empty detect gas remains in inner container 20. As compression air supply 30 continues to compress inner container 20, the empty detect gas is forced through flow passage 42 toward manufacturing process 13. When the empty detect gas passes through empty detect gas sensor 62, empty detect gas sensor 62 sends a signal to system control 46 to turn off compression  
15 air supply 30, thereby terminating operation of system 50. Subsequently, compression air passage 32, gas passage 34, and flow passage 42 are disconnected from empty container 14, empty container 14 is removed from system 50, and a new container 14 containing liquid 12 and headspace gas 18 is connected to system 50. Dispensing of liquid 12 from container 14 then  
20 recommences.

In summary, the purity of some chemicals has a tendency to decay or cross-link when stored for an extended period of time, especially when subjected to temperature fluctuations. To prevent this decay or cross-linking from occurring, an empty portion of the container, referred to as the headspace,  
25 is filled with a headspace gas. The headspace gas prevents the decay of the liquid chemical by inhibiting chemical reactions from occurring in the liquid during storage. When the container is to be connected to a manufacturing process, the headspace gas is no longer needed or desired. Conventional dispensing systems do not allow for the easy removal of the headspace gas prior  
30 to dispensing the liquid chemical. The present invention is a method and system

for dispensing liquid chemical to a manufacturing process from a container including an outer container, an inner container, and a port which communicates with an interior of the inner container, a portion of the inner container occupied by the liquid chemical, a remainder of the inner container occupied by a  
5 headspace gas for preventing decay of the liquid chemical until the container is connected to a manufacturing process. The system includes a probe having a flow passage therein and a gas passage communicating between the interior of the inner container and an exterior of the outer container. The system further includes means in fluid communication with a compression space between inner  
10 walls of the outer container and the inner container for permitting fluid under pressure to flow into the space between the inner walls of the outer container and the inner container to force the headspace gas out of the inner container via the gas passage to a headspace gas drain and to force liquid out of the inner container through the flow passage in the probe to the manufacturing process.

15                 Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.